

Final report of AFOSR project (RD 044076)
“Surface-modified Quantum dots Enhanced luminescence in
Polymer Nanocomposites Light Emitting Diode”

by

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14. ABSTRACT We have prepared highly luminescent dendron-substituted copolyfluorenes that incorporate surface-modified cadmium sulfide nanoparticles. A small percentage of these nanoparticles can be incorporated into the dendritic structures upon tailoring the interfaces between the ligands on the nanoparticles and the dendritic structures in the copolyfluorene. Both the photoluminescence and electroluminescence efficiencies of the polymer nanocomposites are dramatically enhanced&#9472;sometimes by more than double&#9472; relative to the values of the pure polymer, indicating formation of suitable blue-light polymer nanocomposites light emitting diode.					
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Abstract:

We have prepared highly luminescent dendron-substituted copolyfluorenes that incorporate surface-modified cadmium sulfide nanoparticles. A small percentage of these nanoparticles can be incorporated into the dendritic structures upon tailoring the interfaces between the ligands on the nanoparticles and the dendritic structures in the copolyfluorene. Both the photoluminescence and electroluminescence efficiencies of the polymer nanocomposites are dramatically enhanced—sometimes by more than double— relative to the values of the pure polymer, indicating formation of suitable blue-light polymer nanocomposites light emitting diode.

1. Introduction

Conjugated aromatic polymers have attracted a considerable amount of interest over the past few decades because their semiconducting and electroactive properties allow them to be used in a diverse range of applications, such as in batteries, electronic devices, and light-emitting diodes. In particular, the development of blue light-emitting polymers remains critical to the fabrication of full-color organic displays. Polyfluorene^[1–3] layers have emerged as potential sources of blue light for light-emitting diodes because of their relatively high photoluminescence efficiencies.^[4] Indeed, their photo- and thermostabilities are better than those of poly(phenylene vinylene) derivatives.^[5–9] Although these polymers exhibit relatively high photoluminescence quantum efficiencies and good thermal stabilities, their device applications are hampered by their tendency to form aggregates in the solid state. Moreover, most organic chromophores, such as those in polymers, quench to different degrees at various concentrations in the solid state, and this phenomenon leads to broad emission bands and losses in efficiency and purity of color. Attempts at improving the luminescence efficiency of polymers have followed two approaches: steric hindrance approach and the electronic approach. The steric hindrance approach involves altering the interchain distance between polymers by attaching bulky side groups—e.g., dendritic structures—to the main chain of the polymer; such

modifications prevent aggregate formation or concentration quenching. The luminescence efficiencies in these copolymers have been improved in several cases, but this phenomenon occurs in conjunction with a decrease in the molecular weight of the polymers, owing to synthetic yield constraints. The electronic approach involves combining materials having higher quantum yields into luminescent polymers.^[10a] For example, one method combines conjugated organic polymers with wide-band-gap semiconductor nanoparticles.^[10b] Several reports have described^[11–15] the energy levels and electron transport properties of these polymer–nanoparticle nanocomposites; complex phenomena can appear as a result of the sensitivity of the surface ligands and the sizes of the band gaps in the nanoparticles. For instance, the photoluminescence of poly[2-methoxy-5-(ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) can be quenched when nanoparticles are present at a higher concentration, or energy can be transferred from the polymer to the nanoparticles.^[16–18] To the best of our knowledge, however, no one has reported that polymer luminance can be improved by the presence of CdS nanoparticles—possibly because the interactions between these nanoparticles and the polymer segments had not been designed properly or because high concentrations of nanoparticles in a polymer can lead to quenching effects caused by offset band edges between the polymer and the nanoparticles.

In this report, we propose a new approach to improving polymer luminescence by

attaching dendritic structures to polyfluorene (dendritic copolyfluorene) and then incorporating a low percentage of surface-modified semiconductor nanoparticles into the polymer.^[19–20] Dendritic copolyfluorene^[21] contains multiple functional groups that increase both the solubility of the polymer and the number of its interaction sites. By tailoring the interface between the ligands on the nanoparticles and the dendritic structures, a small percentage of the surface-modified cadmium sulfide nanoparticles can be incorporated into the polymer. We have investigated the effect that the addition of these nanoparticle has on the polymer's photoluminescence (PL) and electroluminescence (EL) efficiencies.

2. Results and Discussion

Figure 1 displays the UV–Vis absorption spectra of three differently sized thiophenol-modified CdS (S-CdS) nanoparticles in DMF. The sharp absorption peak at $\lambda = 269$ nm is due to the benzene ring in the thiophenol and the broad absorption peaks at $\lambda = 360$, 410, and 460 nm arise from CdS nanoparticles having diameters of 3, 4, and 7 nm, respectively. The maximum photoluminescence peaks of the S-CdS_{3nm}, S-CdS_{4nm}, and S-CdS_{7nm} nanoparticles in DMF (Figure 2b) occurred at 546, 590, and 655 nm, respectively, when these solutions were excited separately with light at $\lambda_{\text{exe}} =$

360, 410, and 460 nm, respectively. The small peaks at $\lambda = 480, 519, \text{ and } 604 \text{ nm}$, for S-CdS_{3nm}, S-CdS_{4nm}, and S-CdS_{7nm}, respectively, originate from defects on the surfaces of the CdS nanoparticles.

Figure 2 presents the photoluminescence spectra of PF, PF-G0, PF-G1, and PF-G2 recorded in THF. The maximum PL peak of PF-G1, excited at $\lambda_{\text{exe}} = 394 \text{ nm}$, is located at $\lambda = 425 \text{ nm}$; the two additional peaks at $\lambda = 454 \text{ and } 486 \text{ nm}$ are due to vibronic progression of C=C bond stretching. PF, PF-G0, and PF-G1 have nearly equal photoluminescence intensities, which indicates that their fluorophores are well-separated in solution. In comparison, the signal for PF-G2 has about twice the PL intensity, which reflects the larger transition moment arising from the effect of higher conjugation in this dendritic structure.

To more fully understand the photophysics of PF-G1, we investigated films of pure PF-G1 and PF-G1 incorporated with the various-sized S-CdS nanoparticles. We excited the samples using a broadband ($\Delta\lambda = 10 \text{ nm}$) xenon lamp having a central wavelength of 394 nm and a narrow-band GaN diode laser. Figure 2(b) displays the results of this study. We observed clear vibronic features at 425, 445, 472, 508, 544, and 598 nm for all of the PF-G1 films. In particular, the first three of these vibronic peaks overlap with the $1s_e-1s_h$ exciton absorption peaks of S-CdS_{4nm} and S-CdS_{7nm} quantum dots. Hence, it appears that the only possible energy transfer in this case is

from PF-G1 to the CdS nanoparticles, but this situation requires further confirmation.^[22] In addition, the broad absorption features of the S-CdS quantum dots that appear below 400 nm may also improve the photon absorption efficiency of the composite films.

Figure 3 displays the PL spectra of PF-G1 thin films containing the different-sized S-CdS nanoparticles. We controlled the thicknesses of these films to within 53–56 nm, as measured using an α -step instrument. When excited using a xenon lamp at 394 nm, the main PL peaks for these nanocomposites are located at the same wavelength as that of pure PF-G1, but the intensities of these peaks are affected dramatically by the amount and size of the incorporated S-CdS. For instance, in Figure 3a we observe that when 4 wt% of S-CdS_{3nm} nanoparticles are added to PF-G1, the intensity of the PL peak at 425 nm increased by more than 2.5 times relative to that of pure PF-G1. This effect becomes more pronounced as the size of CdS nanoparticles increases, as illustrated in Figures 3b and 3c. The intensities of the peaks at 425 nm of the PF-G1 thin films incorporating 4- and 7-nm-diameter CdS nanoparticles increased by 3.1 and 3.4 times, respectively, relative to that of pure PF-G1. We did not observe any peaks between 500 and 700 nm for S-CdS nanoparticles present in PF-G1, presumably due to the low S-CdS concentration that we used. The intensity of the PL peak at 425 nm in 4 wt% S-CdS_{7nm}/PF-G2 was more than 3 times that of pure PF-G2, with no appearance

of the CdS PL peak (see the supporting information). To fully understand this behavior, we performed two control experiments. The first considered the light emission of the S-CdS nanoparticles; the second was concerned with whether other luminescent polymers lacking dendritic structures behave in a similar manner. Figure 4 illustrates that no detectable PL peaks appeared when the same amount (4 wt%) of S-CdS was present in optically inactive poly(methyl methacrylate) (PMMA). Moreover, the addition of the same amount of S-CdS nanoparticles into PF-G0 and MEH-PPV did not substantially change the intensities or locations of the PL peaks of these polymers. This finding indicates that the CdS nanoparticles themselves emit relatively weak light in the nanocomposites, if at all. What is more interesting, however, is the role that CdS plays in the PL enhancement of the dendritic polymers. There are two possible mechanisms through which CdS nanoparticles enhance the PL of copolyfluorene, i.e., through steric hindrance or through electronic phenomena. The first of these mechanisms proposes that an increase in the inter-polymer chain distance in the nanocomposites leads to a decrease in dimer formation. In the pure PF-G1 polymer, dimers form as a result of the close proximity of polymer chains when they are excited. The inter-polymer chain distances in the S-CdS/PF-GX ($X = 1, 2$) nanocomposites increases upon incorporating the S-CdS nanoparticles into the dendritic polymers. Figure 5A shows X-ray diffraction spectra of S-CdS/PF-G1

obtained by deducting the glass substrate background (i.e. the difference between polymer on substrate and substrate).^[23] The packing of PF-G1 chains in the solid state was found to be amorphous by X-ray diffraction experiments, with two broad correlation peaks. The peak that remains at $2\theta = 20.1^\circ$ (d -spacing = 4.4 Å), despite the variation in the amount of CdS nanoparticles, is due to the average C-C intermolecular distance (i.e. the distance between the pendent group of the polymer chains) of PF-G1, while the other peak at lower diffraction angle that changes with the amount CdS nanoparticles is a measurement of the average inter polymer chain distance as reported in a previous study of dendritic polyfluorene.^[24] Figure 5B shows that the average inter-chains distance of PF-G1 in the nanocomposite increases with the amount of CdS nanoparticles. For instance, in the presence of 4wt% CdS_{4nm} nanoparticles, the inter-chain distance in PF-G1 increases to 28.5 Å from 12.6 Å for pure PF-G1. As the CdS in PF-G1 increase to 8%, the peak shifted to a diffraction angle smaller than the limit of the X-ray instrument and seemed to suggest that the polymer chains are further apart, indicating that disordering of polymer chains could have happened (i.e. polymer chain solid packing break). One of the reasons that inter-chain distance increase in the presence of CdS nanoparticles is possibly due to the selective distribution of the nanoparticles into the dendritic regions of the structure, which results from the relatively strong interaction between the benzyl groups of the dendrons and the phenyl

groups of the thiophenol ligands of CdS (Scheme 1). Figure 5C presents the Fourier transform infrared (FTIR) spectra of PF-G1 and the PF-G1 nanocomposite containing 4 wt% CdS_{4nm}. In comparing these two spectra, we detect several significant differences that originate from the addition of the S-CdS nanoparticles. The features near 500 cm⁻¹ may be due to low-frequency ring bending and deformation modes. The peaks near 990 cm⁻¹ are due to the breathing mode of the benzene ring, and the peaks near 1600 cm⁻¹ originate from C=C stretching. The inclusion of S-CdS nanoparticles significantly quenches the deformation and breathing modes for the benzene rings; this observation indicates that there is a possibility that π - π stacking occurs to a large extent between the phenyl groups of thiophenol and the dendritic units in PF-G1. The interactions between aromatic rings via π -stacking (i.e. the van der Waals contact between aromatic ring)^[25] are at the origin of many phenomena of organic material science^[26] and biological chemistry,^[27] and can be determined by the oxidation potential of the material during electron detachment. Another piece of supporting evidence of CdS nanoparticles bound to the dendrons can therefore be found in the oxidation potential change, when the π -stacking of thiophenol surfactant on CdS with the phenyl groups in the dendron structure occurs. Figure 5D shows that both the onset and the true oxidation potential ($E^{1/2}_{ox}$) of S-CdS/PF-G1 decrease with the increasing amount of CdS. For example, in the presence 8 wt % CdS_{4nm}

nanoparticles, the oxidation potential, $E^{1/2}_{ox}$, of the composite reduced to 1.30V from 1.37V for pure PF-G1. The cutoff potentials for these materials are all at 2.20V, and their curves are reversible after three scans at a scanning rate of 50 mV/s. While the oxidation potential change for PF-G1 by CdS is small due to the actual volume percentage of CdS in PF-G1 is one fourth of its weight percentage (density of CdS vs. PF-G1 is close to 4:1), it is significant in the sense that this different electrochemical behavior indicates a weak interaction between PF-G1 and S-CdS, in which one of the possible causes is due to the π - π interaction between thiophenol and the dendritic units. The phenomenon is consistent with a report by Curtis et al ^[28] that π -stacked structures between small molecules may provide higher carrier mobilities and lower oxidation potential. Hence, our data implies that there is a possibility that some portions of the ligands of CdS nanoparticles and the dendritic structure of copolyfluorene formed π -stacked structure, resulting in greater chain separation.

By combining the FTIR, oxidation potential, and X-ray diffraction results, it can reasonably be concluded that there exists a possibility that the incorporation of some of S-CdS nanoparticles into certain dendritic polyfluorene chains, and that leads to increased distance between some parts of polyfluorene chains. In spite of the fact that greater copolyfluorene chain separation might reduce charge transport somewhat in the

device, the actual charge transport was enhanced as evidenced in the current density vs. voltage data in Figure 8b, where the current density of copolyfluorene increased substantially (almost 50% at 8V) in the presence of 8wt% S-CdS nanoparticles. This phenomenon might result from an enhancement of charge transport by CdS nanoparticles and the π -stacked structure in the device that is far larger than the adverse effect caused by the polymer chain separation. This phenomenon implies that the free volume in the nanocomposites is larger than that of the pure polymer because the inter-polymer chain distance is a one-dimensional representation of the free volume. The glass transition temperatures (T_g) of the S-CdS/copolyfluorene nanocomposites at various compositions are summarized. (see the supporting information). Our hypothesis is supported by the fact that the value of T_g for 8 wt% S-CdS/PF-G1 is depressed to 74.3 °C from 90.5 °C for pure PF-G1. We also found that the values of T_g decreased upon increasing the diameter of the S-CdS nanoparticles. The depression is also apparent in the case of the PF-G2 nanocomposites (from 59.1 for pure PF-G2 to 54.3 °C); the low value of T_g of PF-G2, relative to that of PF-G1, is due to the presence of a greater number of chain ends in the second-generation dendron. Figure 6 displays transmission electron microscopy (TEM) images of 4 wt% S-CdS/PF-G1; it is clear that the S-CdS nanoparticles did not form large aggregates in the PF-G1 matrix. The other possible mechanism for the

increased luminance results from electronic interactions occurring between CdS and PF-G1, but this type of interaction is difficult to verify because of the low concentration of nanoparticles in PF-G1. Thus, in this study, we found no evidence for energy transfer occurring from PF-G1 to the CdS nanoparticles.

To obtain a quantitative assessment of the luminance enhancement, we used Beer's law to determine the normalized luminescence efficiency of these nanocomposites. Table 1 lists the values of the normalized photoluminescence with respect to the molecular concentration. Substantial improvements in the photoluminescence of the composite systems occurred when a small weight percentage of S-CdS nanoparticles was present in either PF-G1 or PF-G2. For instance, we found a two fold improvement in the photoluminescence per fluorene chromophore for 4 wt% S-CdS/PF-G1 relative to that of pure PF-G1 (i.e., the quantum yield increased from 0.22 to 0.46). For the second-generation dendritic polymer nanocomposite, S-CdS/PF-G2, the photoluminescence per fluorene chromophore increased by more than 1.8-fold relative to that of pure PF-G2 (i.e., the quantum yield increased from 0.55 to 0.99). This phenomenon can be explained quantitatively using the equation^[29]

$$\Phi_{\text{PL}} = \Phi_{\text{FL}} / \Phi_{\text{A}} = k_{\text{r}} / (k_{\text{r}} + k_{\text{nr}}) \quad (1)$$

where Φ_{PL} is the fluorescence yield, Φ_{FL} is the number of photons emitted, and Φ_{A} is the number of photons absorbed. The terms k_{r} and k_{nr} represent the rates of decay of the radiative and combined non-radiative processes, respectively. The S-CdS nanoparticles in PF-G1 cause a decrease in k_{nr} , which in turn results in an increase in Φ_{PL} . The observation that the incorporation of CdS nanoparticles into the dendritic polymer structures reduces the degree of energy transfer from the isolated polymer chains to an inter-chain dimer is also evident in the electroluminescence of the S-CdS/PF-G1 device. We fabricated double-layer LED devices having the configuration ITO/PEDOT:PSS/polymer/Ca/Al, where PEDOT:PSS [poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (Batron-P 4083)] was used as the hole injection/transporting layer at a thickness of 150 nm. A thin layer of Ca (35 nm) was employed as the cathode, which was coated with a 180-nm-thick layer of Al. The thickness of the emissive layer was ca. 80 nm. Figure 7 displays the normalized electroluminescence of the devices. The similarities between the EL and PL spectra of both the pure PF-G1 and S-CdS/PF-G1 devices indicate that the same excitation processes occur in each case. The EL device prepared from pure PF-G1 emits blue light at 426 nm and a weak green light in the range 465–550 nm. In the case where 8% S-CdS was incorporated into PF-G1, the green emission in the range 465–550 nm reduced sharply, while the peak at 426 nm

became a sharper and major emission peak. In addition, the full width at the half-maximum (FWHM) of the peak of 8% S-CdS/PF-G1 reduced to 49 nm from a value of 112 nm for pure PF-G1, indicating that it emits a purer blue light. Compared with its PL spectrum, the change in relative intensities in vibronic structure indicates that aggregate emission is dominant in its EL process.^[30–31a] This behavior has also been observed in polyfluorene derivatives, namely for PF-POSS.^[31b] Figure 8 displays the variations of the current density and brightness of the EL devices. The turn-on voltage increased to 4.5 V for PF-G1 containing 8% S-CdS from 4 V for the pure-PF-G1 EL device. A more-than-fourfold increase in the maximum brightness of the 8% CdS/PF-G1-based device occurred relative to that of the pure-PF-G1 EL device (1196 vs. 298 cd/m²) at a drive voltage of 8 V and a current density of 564 mA/cm². These improvements are probably due to the lower degree of aggregation that occurred upon incorporating S-CdS into PF-G1.

3. Conclusions

Placing a small amount of surface-tailored CdS nanoparticles into the dendritic structure of copolyfluorene substantially improves the efficiency of the polymer's light emission as well as the purity of the emitted light. One possible explanation of the enhancements in photoluminescence and electroluminescence may probably be

due to a reduction in the concentration of inter-polymer excimers through which energy transfer occurs from the excited polymer chains to their neighboring ground state polymer chains; i.e., the CdS nanoparticles caused an increase in the inter-polymer chain distance.

4. Experimental

Surface-modified CdS nanoparticles were synthesized by reacting cadmium acetate dihydrate [$\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$], sodium sulfide (Na_2S), and thiophenol (HSC_6H_5) in methanol at room temperature, using a variation of the kinetic trapping method.^[32–33]

The diameters of the synthesized CdS can be adjusted by changing the ratio of the three ingredients. These CdS nanoparticles are termed “S-CdS” nanoparticles, indicating that the surface ligands on the CdS nanoparticles are thiophenol units.

After filtration, the S-CdS nanoparticles were collected and then dispersed in DMF.

From the absorption edge (λ_c) in their UV–Vis spectra, the S-CdS nanoparticles were determined to have diameters of ca. 3, 4, and 7 nm.^[34–35]

The synthesis of the dendritic polyfluorene was performed using a typical Suzuki coupling reaction protocol. The copolymerization of dendritic monomers and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was

performed using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst and Aliquat 336 as a phase-transfer reagent in a mixture of toluene and aqueous potassium carbonate (2.0 M). A detailed description of the synthesis of these dendritic copolyfluorenes is available elsewhere.^[21, 36] The copolymers were named PF-GX, where X represents the number of generations of the dendron (X = 0, 1, or 2). S-CdS/DMF was added to a previously prepared dendritic copolyfluorene PF-GX (X = 0, 1, 2) in DMF solution and stirred overnight. PF-G1, the polyfluorene possessing one dendron generation, had a weight-average molecular weight (M_w) of 65 kDa and a polydispersity of 1.9; PF-G2, the polyfluorene having two dendron generations, had a M_w of 40 kDa and a polydispersity of 2.2. The mixture of S-CdS/PF-GX in DMF was dried under vacuum at 313 K for 2 h and then maintained at 383 K for another 24 h to obtain the S-CdS/PF-GX nanocomposite film. Scheme 1 outlines the synthesis of the nanocomposites formed from the thiophenol-modified CdS nanoparticles and the dendritic copolyfluorenes. Gel permeation chromatographic analyses on samples were performed with a Waters 410 Differential Refractometer and a Waters 600 controller (Waters Styragel Column). All GPC analyses of polymers in THF solutions were carried out at a flow rate of 1 mL/min at 40 °C; the samples were calibrated using polystyrene standards. The current–voltage characteristics were measured using a Hewlett–Packard 4155B semiconductor parameter analyzer. The

power of the EL emission was measured using a Newport 2835-C multi-function optical meter. The brightness was calculated using the forward output power and the EL spectra of the devices; a Lambertian distribution of the EL emission was assumed. Cyclic voltammetry (CV) measurements were performed with an Autolab ADC 164 electrochemical analyzer in anhydrous acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scanning rate of 50 mV/s. The working and auxiliary electrodes were platinum. The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode with ferrocene as the internal standard. Thin films of polymer were prepared by a solvent casting method. Blank CV experiments were carried out in fresh buffer solutions, and these were determined to be electrochemically inactive.

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Figure Captions:

Figure 1: Normalized UV–Vis absorption spectra recorded in DMF for S-CdS nanoparticles having three different diameters.

Figure 2: (a) Photoluminescence spectra of PF [poly-2,7-(9,9-dioctylfluorene)], excited by a xenon lamp at $\lambda_{\text{max}} = 394$ nm, and PF-G0, PF-G1, and PF-G2, all recorded in THF at the same concentration (5×10^{-6} M). (b) Photoluminescence spectra recorded in DMF of (i) PF-G1 in the solid state, using a xenon lamp as the excitation light source, (ii) PF-G1 in the solid state, using a GaN diode laser, and (iii) S-CdS nanoparticles having three different diameters.

Figure 3: Photoluminescence spectra of thin films of (a) S-CdS_{3nm}/PF-G1, (b) S-CdS_{4nm}/PF-G1, and (c) S-CdS_{7nm}/PF-G1, normalized with respect to the PL intensity of PF-G1.

Figure 4: Photoluminescence spectra of thin films of (a) pure PF-G0, (b) PF-G0 containing 4 wt% S-CdS, (c) pure MEHPPV, (d) MEHPPV containing 4 wt% S-CdS, and (e) PMMA containing 4 wt% S-CdS.

Figure 5: **A.** X-ray diffraction spectra of S-CdS/ PF-G1 nanocomposite. (a) PF-G1 (b) PF-G1 containing 3 wt% S-CdS, (c) PF-G1 containing 4 wt% S-CdS, and (d) PF-G1 containing 8 wt% S-CdS. **B.** The effect of the amount of S-CdS on the Bragg d spacing of PF-G1. **C.** FTIR spectra of (a) PF-G1 and (b) PF-G1 containing 4 wt%

S-CdS. **D.** Cyclic voltammogram of the oxidation of polymer.

Figure 6: Transmission electron microscopy images of PF-G1 films containing (a) 3 wt% and (b) 4 wt% of S-CdS.

Figure 7: Normalized electroluminescence spectra of devices prepared from S-CdS/PF-G1 in the configuration ITO/PEDOT/polymer/Ca/Al.

Figure 8: (a) I–V and (b) L–V curves of devices prepared from S-CdS/PF-G1 in the configuration ITO/PEDOT/polymer/Ca/Al.